



Zurück



A new mineral flame retardant with increased thermal stability

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Abstract

Flame retardants (FR) are essential parts in plastics to improve fire resistance. Compared to organic FR, i.e. halogen, phosphorus or nitrogen containing materials, inorganic mineral FR, such as aluminiumhydroxide (abbr. ATH; aluminiumtrihydrate) or magnesiumhydroxide, have gained an increased interest in the past few years.

ATH, the dominating mineral FR in terms of annual consumption, has limited applications due to thermal decomposition starting at temperatures around 200°C. For polymeric materials exceeding processing temperatures of 200°C, only a few mineral FR are available on the market. The most important product out of this group is magnesiumhydroxide with a thermal stability up to 320°C. To offer alternatives based on ATH, Nabaltec has developed a new mineral FR with an onset of decomposition at around 280°C. The chemical name of this compound is boehmite (tradename: Apyral® AOH 180 DE) with the formula AlOOH .

This paper gives a detailed survey on the new product Apyral® AOH 180 DE, its production, properties and applications. Physical characteristics of boehmite filled halogen-free cable compounds in comparison to magnesiumhydroxide will be shown.

Introduction

In the past decades polymeric materials have entered almost every part of our daily life. A key for the success was the development of new and improvement of existing plastics covering a broad range of properties. Although the consumption of plastics is already impressive, in the last years there has been even a faster growth in the use of composite materials. Composites are chosen when it's beneficial to combine positive properties of two or more materials, e.g. polymer and filler. Some reasons for the addition of functional fillers to polymer compounds are (extract):

- Improve abrasion resistance;
- Increase stiffness;

- Reduce shrinkage;
- Improve processability;
- Hardness;
- Increase compressive strength;
- Change electrical properties;
- Fire resistance.

Most of these property enhancements can be achieved by the choice of appropriate mineral fillers. In addition plastics have to be stabilized extensively in order to protect them over their life time against e.g. chain degradation caused by UV radiation or heat. Another extremely important subject is fire resistance, as most commercial plastics burn fairly easily even under moderat conditions.

Therefore it's common practice to use FR for improving the fire resistance performance and reducing the tendency for smoke emission. Today a variety of different FR are available on the market which are often tailormade for specific applications. This enables customers to chose the most suitable grade/masterbatch directly and thus avoiding expensive own investigations.

Traditionally organic FR contain elements like chlorine, bromine, phosphorus, nitrogen and antimony. The advantage of these FR is that often only the addition of a few percent is sufficient to improve the fire retardancy behaviour significantly. Although they are very effective, some of them cause serious trouble in case of fire. The combination of halogen and antimony oxide, for instance, is coming under certain pressure due to environmental issues such as the evolution of smoke and toxic gases.

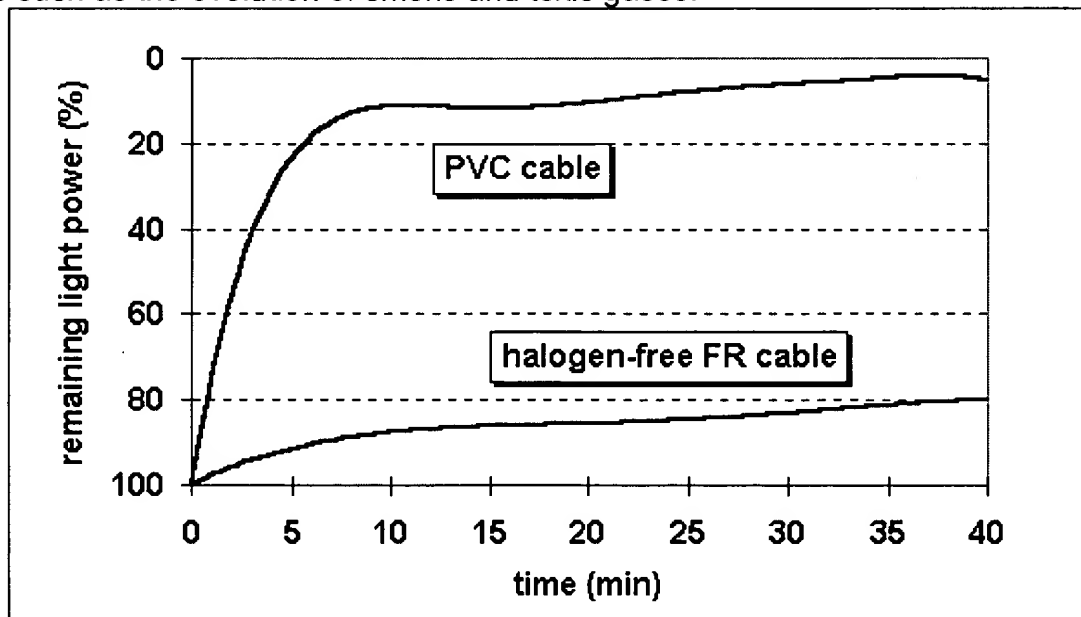


Fig. 1. Smoke density of halogen-free cable vs. PVC cable.

For many years metalhydroxides have been established to substitute critical organic FR in applications where the human life is directly threatened in a fire. The halogen- and acid-free character of such substances in combination with halogen-free plastics is promoting and pushing the trend to use environmentally benign products. During combustion metalhydroxides don't evolve toxic or corrosive gases as well as remarkably suppressing the emission of smoke.

By far aluminiumhydroxide is the dominant product in use today. In recent years price reduction has strengthened its position on the market. Various grades of different grain size distributions (ground or fine-precipitated) have been developed to meet all possible requirements. The limitation of ATH is the relatively low decomposition temperature starting around 190 to 200°C; hence ATH can't be used in polymers which are processed above or close to this level such as polyamide or common polypropylene.

With a thermal stability up to 320°C, magnesiumhydroxide (abbr. MGH) is the material of choice for such applications. It acts in a similar manner to ATH but there is no direct competition between both products as typical prices for suitable MGH grades are almost double of the ATH level.

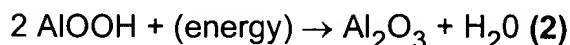
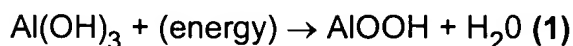
Metalhydroxides have to be added to plastics in a substantial amount in order to impart a significant increase in fire resistance behaviour. Typical values are between 55 and 65 wght.-% depending on the polymer system, consequently we are talking about a composite. Due to the high filler content the melt viscosity will rise to an extent where commercial processing, esp. in continuously running systems such as twin screw extruders or BUSS kneaders, becomes very difficult and may affect the ability to yield a homogenous compound.

A typical cable and wire material like PE/EVA with 60 wght.-% of ATH is processed at temperatures up to 195°C. In order to cut costs, today everybody is looking to reduce processing time and increase the output. This is directly linked with the rheological condition in the system. As the addition of processing aids is limited, an increase in temperature is sometimes the only possibility. By doing that, ATH would decompose during compounding and consequently it has to be replaced by MGH. Hence MGH is currently used more often in polymer systems which previously have been dominated by ATH.

As MGH is without direct competition within this thermal stability range, some years ago Nabaltec have launched a project with the aim to produce a mineral FR based on ATH which has a similar onset of decomposition as MGH. It took several years of development with countless trials to create finally a new material possessing all required characteristical properties. Chemically spoken it's an aluminiumoxidhydroxide named boehmite with the formula AlOOH . Nabaltec's tradename for this material is Apyral® AOH 180 DE.

Production of boehmite

Boehmite is a stable thermodynamic intermediate of the thermal conversion from aluminiumhydroxide to alumina according to following equations:



Aluminiumhydroxide is produced from bauxite ore by the Bayer process. The process includes digestion of bauxite at elevated temperatures with hot caustic soda under pressure to solubilize the alumina as sodium aluminate, separation of insoluble impurities (so called red mud) and subsequently the precipitation of ATH.

The thermal treatment of ATH acc. to equ. (1) can be carried out either with the dry ATH powder or in an aqueous ATH suspension. In order to receive a boehmite with a mean particle size around 1 μm and moderate specific surface area's lower than 20 m^2/g , which is required in cable and wire applications, the raw material ATH must have a similar grain size distribution. Several trials have shown that complete conversion of fine ATH powder using a drying chamber leads to boehmite grades with tremendously high specific surfaces around 150 m^2/g . This is an unacceptable value for most purposes.

In contrast the hydrothermal conversion of an aqueous ATH suspension in an appropriate pressure stable equipment (autoclave or tube reactor) at temperatures around 230°C is generating a boehmite grade with grain parameters and a specific surface within desired range.

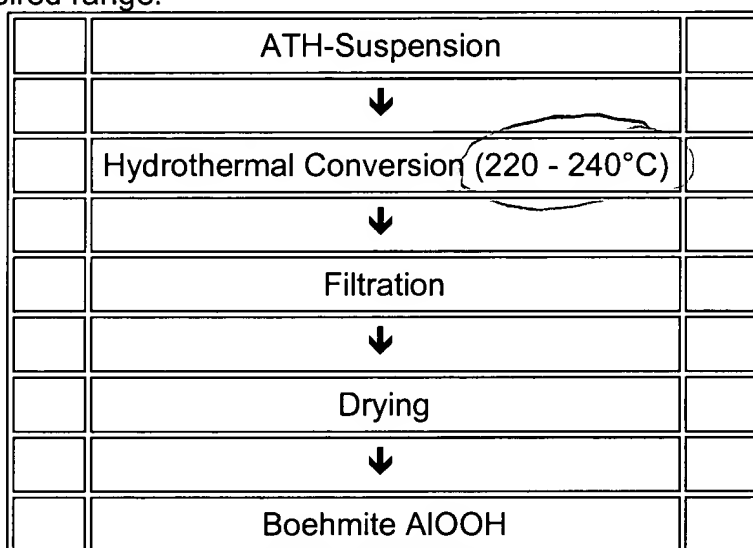


Fig. 2. Flow chart of Nabaltec's boehmite production.

Product characteristics of Apyral® AOH 180 DE

Nabaltec is using a fine precipitated ATH with mean particle size around 1 μm and a specific surface between 4 to 9 m^2/g for conversion in tube reactor. The dehydration reaction during the hydrothermal treatment causes grain fragments hence leading to slightly finer boehmite particles with a specific surface area between 15 and 18 m^2/g . This second refinement after the precipitation process of ATH forms an unbelievably pure and homogeneous material characterised by parameters listed in Tab. 1.

Tab. 1. Characteristics of Apyral® AOH 180 DE.

parameter	unit	approx. value
Na ₂ O	%	0,05
SiO ₂	%	0,02

loss on ignition [110-1100° C]	%	17
mean particle size	μ m	0,6
Specific surface area	m ² /g	16
moisture	%	0,5
sieve residue >45μm	%	0,01
specific conductivity	μ S/cm	100
whiteness	%	98

As illustrated in Tab. 1, Apyral® AOH 180 DE fulfills all criterias which are crucial for thermoplastic and elastomeric applications. The cable industry is especially always interested in FR mineral fillers with extremely low specific conductivities. One further advantage is that Apyral® AOH 180 DE also possesses an almost neutral surface condition (pH of an aqueous suspension around 8) in comparison to MGH. The more alkaline surface character of MGH may cause dispersion problems during compounding due to unwanted interactions with organic formulation ingredients. Therefore most MGH have to be surface treated at least with an fatty acid to overcome these disadvantages. Unlike MGH Apyral® AOH 180 DE can be processed without surface treatment and shows an easier powder handling as well.

Due to the dehydration process during the hydrothermal treatment, boehmite has lower weight loss on ignition than ATH. This is illustrated in Fig. 3.

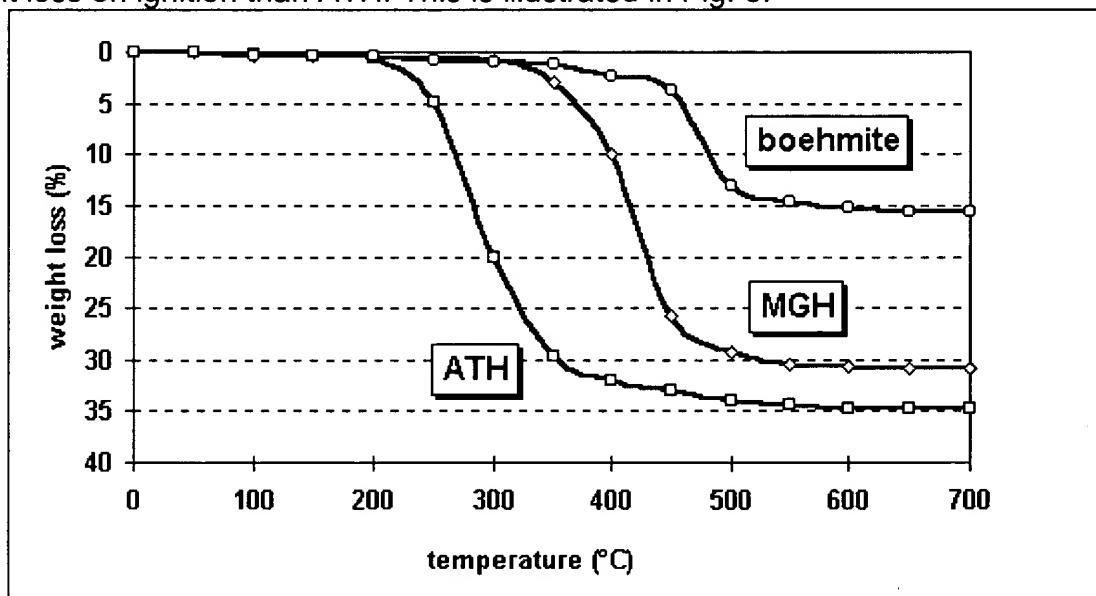


Fig. 3. Loss on ignition of ATH, MGH and boehmite (heating rate 5°C/min).

The theoretical loss on ignition of boehmite amounts to 15 %, compared to 31 % for MGH and 34,6 % for ATH. Due to this significant difference, the contribution of Apyral® AOH 180 DE to the over all flame retardance behaviour is lower compared to both other minerals, however it's still

an effective and versatily useable material for many applications and hence a valuable alternative to MGH in the upper thermal stability range.

Application

It's an increasing tendency to promote and use halogen-free flame retardant (abbr. HFFR) materials in areas where - in case of fire - personal injury, death or property damage can occur. This focuses mainly on the substitution of halogenated material such as PVC due to their aggressive and toxic decomposition products. Possible alternatives to PVC, i.e. for cable compounds, are based mainly on polymer grades like polypropylene copolymers (PP) or polyethylene/ethylene vinylacetate (PE/EVA) and usually have a mineral FR content of 60 to 65 wght.-%.

Due to its product characteristics Apyral® AOH 180 DE can be added to compounds similar to MGH or ATH. If processed thoroughly a well dispersed compound with balanced physical properties can be achieved.

Typical applications with characteristic properties for HFFR cable compounds are shown below.

Experimental and testing

Homogeneous compounds were prepared by means of an internal mixer (Brabender). Test specimens were cut out sheets which were obtained by compression molding with heated plates. For flame retardancy rating limiting oxygen index (LOI) was determined according to ASTM D 2863-77 using 3 mm specimens. Mechanical properties were achieved by stress-strain experiments according to DIN 53504. Melt flow index (190°C, 21,6 kg) was carried out according to ASTM D 1238.

The magnesiumhydroxide grade used for these investigations was a very pure, synthetic, high quality material with a mean particle size around 0,8 µm and a specific surface area of 10 m²/g.

- Thermoplastic Polypropylene Compound

The detailed formulation is prohibited to state as this is subject to a secrecy agreement. However the compound consists of a common PP-copolymer filled with 60 wght.-% of corresponding mineral FR and some other additives (stabilizers) in minor amounts.

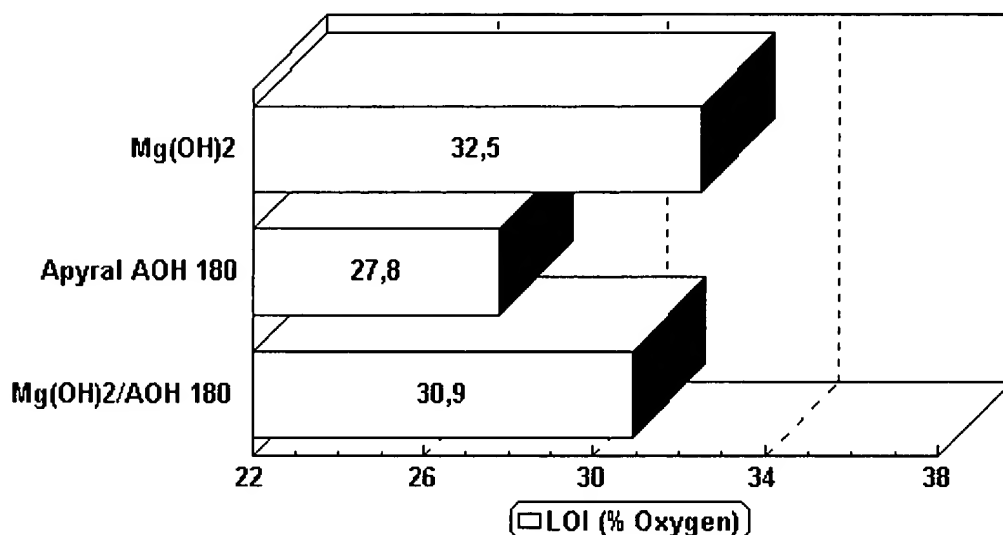


Fig. 4. LOI-values of PP compounds filled with MGH, Apyral[®] AOH 180 DE and a 50:50 blend (w/w) of both mineral FR.

As illustrated in Fig. 4, the LOI-value drops from 32 % to 28 % when replacing MGH with boehmite. One reason for that may be related to the lower amount of chemically bonded water released during combustion (see also Fig. 3) and hence a decreased dilution of the oxygen concentration supporting the burning process. Nevertheless an LOI of 28 % can be enough for PP-application which doesn't match the most stringent flammability classifications. If required boehmite can be blended with MGH (i.e. 50:50 blend) with the aim to improve the fire resistance behaviour to a sufficient level for many cable applications. It's imaginable that tailor-made blends with different compositions can be offered in the near future.

Fig. 5 describes some mechanical properties of the various PP compounds.

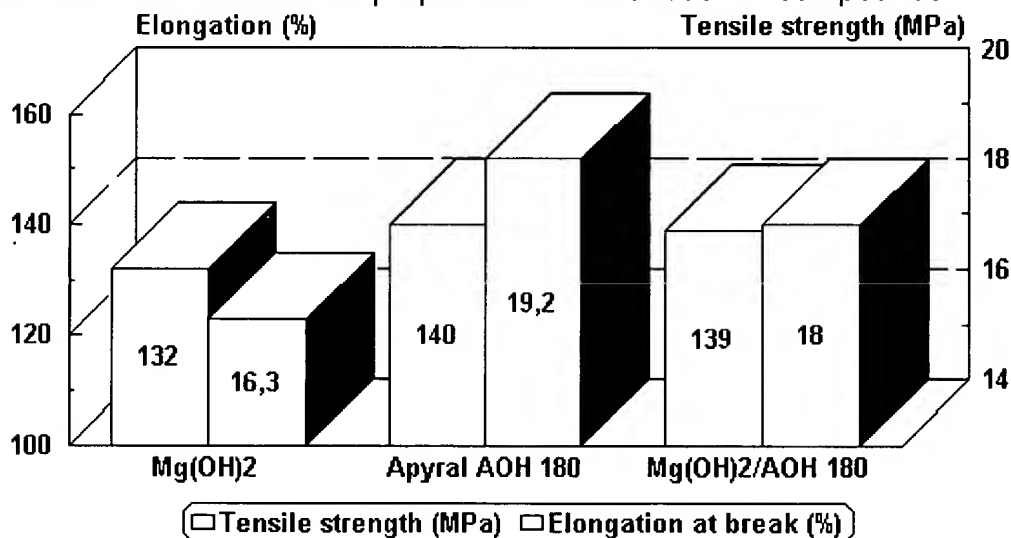


Fig. 5. Mechanical properties of PP compounds filled with MGH, Apyral[®] AOH 180 DE and a 50:50 blend (w/w) of both mineral FR.

In terms of practical requirements tensile strength and elongation shouldn't be below 10 MPa and 125 %, resp. Although the MGH filled compound exceeds both levels the values of the Apyral® AOH 180 DE filled plastic are significantly improved which additionally guarantees a certain compounding safety. Even the compound with the 50:50 mineral blend shows advanced mechanical data compared to the MGH compound.

- PE/EVA Compound

For cable applications, it's a common practice to incorporate EVA to highly filled polyolefines such as PE composites. Due to the chemical composition and structure, EVA improves both the electrical performance and the fire resistance behaviour. By choosing EVA grades with increasing vinylacetate content within the polymer chain both properties can be further enhanced. In the same direction the price for EVA raw material rises as well which is counteractive aspect.

Tab. 2 shows data of compounds filled with both Apyral® AOH 180 DE alone and a blend of Apyral® AOH 180 DE / MGH with the ratio 4 parts boehmite to 1 part MGH. A typical PE/EVA formulation has been used which in order to reduce the rheological level and hence increase the throughput can be processed also at temperatures exceeding 200°C.

Tab. 2 Typical PE/EVA formulation with corresponding compound properties.

	filler content 60 wght.-%		filler content 65 wght.-%	
Formulation	boehmite	boehmite/MGH	boehmite	boehmite/MGH
Escorene LL 104 YB	9,66	9,66	4,66	4,66
Escorene UL 00226	29	29	29	29
Vinylsilan	1	1	1	1
Interox TMCH 75-AL	0,04	0,04	0,04	0,04
Irganox 1010	0,3	0,3	0,3	0,3
Apyral® AOH 180	60	48	65	52
Mg(OH)2	-	12	-	13
Results				
Tensile strength (MPa)	14,8	16,2	18,2	16,5
Elongation at break (%)	194	173	157	129

LOI (% oxygen)	28,9	32,9	31,2	37,0
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For this formulation, an EVA grade with 26 % vinylacetate (Escorene UL 00226) has been selected, generating a sufficiently flame retarded compound by incorporating only Apyral® AOH 180 DE (60 wght.-%). A further addition of 5 wght.-% boehmite raises the level up to 31 % and at the same time keeping the mechanical properties balanced on an elevated level. As expected, by substituting 20 % of the total mineral part with MGH, the improvement regarding the flame retardancy is already obvious. However esp. for the highly filled compound (65 wght.-% mineral FR) this correlates again with a drop in physical properties.

- EVA Compound

The following basic EVA formulation consists of Escorene UL 00119, an aminosilan as phase compatibilizer and varying Apyral® AOH 180 DE contents. Tab. 3 depicts characteristic physical properties.

Tab. 3. Compound properties of a typical EVA formulation.

	Apyral® AOH 180 DE content (wght.-%)		
	55,4	61,3	69,3
Tensile strength (MPa)	18,6	18,2	16,3
Elongation at break (%)	254	165	98
Melt flow index (cm ³ /10 min)	1,7	0,5	0,1
LOI (% oxygen)	28,0	34,6	41,4

This example shows that even LOI values beyond 40 % can be reached by the addition of Apyral®

AOH 180 DE only. However the viscosity behaviour during compounding as well as the elongation at break is deteriorated substantially. However it has to be pointed out that this is a very basic recipe and further experiments must be carried out to find suitable ingredients such as processing aids and compatibilizers, so the weak parameters may be lifted again to an acceptable level.

Tendency of Apyral® AOH 180 DE to promote char formation

Among others, one important factor rendering mineral fillers to flame retardants is their contribution to the self-extinguishing character of composite materials in case of fire. An essential part within this effect is linked with the ability to form a mechanically stable and non-combustible char (consisting of corresponding oxide) on the surface of the plastic during decomposition which impedes the thermal feedback (attack of heat and oxygen).

Several fire test's (UL 94, LOI, large scale fire test's) of Apyral® AOH 180 DE filled

plastics have shown that the tendency of boehmite to form such protective chars is extremely pronounced compared to both compounds including ATH or MGH. In addition to that, residual inorganic material increases in volume generating an expanded barrier with almost closed cell structure. This blowing effect, which is an important criteria for intumescent fire retardants, renders Apyral® AOH 180 DE to a very effective flame retardant showing its performance mainly in large scale fire test's.

An explanation for this effect becomes difficult due to the lack of comprehensive studies so far. Forthcoming investigations will focus on this issue to understand this behaviour in more detail.

Conclusion

As shown in this paper, the recently developed Apyral® AOH 180 DE can be versatily used as an effective and worthwhile mineral flame retardant filler for plastics in the temperature range beyond 200°C. Despite only a minor content of chemically bonded water, Apyral® AOH 180 DE displays its real flame retardant performance in large scale fire test's due to the tendency to form a stable, non combustible layer during decomposition. In high end applications with stringent fire resistance requirements magnesiumhydroxide has still some advantages. Consequently the main tasks for the near future are to form customer oriented projects with the target to overcome these problems either when using Apyral® AOH 180 DE alone or in specific blends with magnesiumhydroxide.

There is still a huge potential for this material in various other areas such as polyamide. Nabaltec's philosophy and intention is to identify these new applications and adapt this material in terms of market needs.

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DAVICAT® Aluminas are available in many forms. Beads range from 0.7 - 1.4 mm in diameter with surface areas of 130 and 220 m²/g and pore volumes up to 1.2 cc/g. Extrudates range from 0.5 to 1.25 mm, with various pore size distributions.

Alumina supports are typically prepared by precipitating sodium aluminate with or without a cation and alum to yield a doped pseudo-Boehmite material. Subsequent calcinations in the manufacturing process can change the phase of the alumina (e.g., to theta or gamma). The supports can be treated for excellent stability at high temperatures to avoid agglomeration/sintering of surface metals.

Catalytic Features

- Amphoteric material
- Chromatographic, choice of cation addition modifies the type and strength of acid sites
- Many crystalline forms possible
- Pore shape and size easily modified
- Surface Area: 10-400 m²/g
- Pore Volume 0.1-1.8 cc/g
- Appropriate for intermediate pH.

Example Reactions which use Alumina as a Support:

- Ammonia Synthesis
- Benzene by Disproportionation of Toluene
- Dehydrogenation of Butane to Butadiene
- Synthesis of Caprolactam
- Selective Hydrogenation of Phenol to Cyclohexanol
- Synthesis of Ethylene by Propylene Disproportionation
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A preparation method for pseudo-boehmite and gamma-alumina

Patent Number: CN1250746A

Date of Patent:

Inventor(s): Yang Qinghe (CN); Li Dadong(CN); Shi Yahua(CN); Zhuang Fucheng (CN); Liu Bing(CN); Kang Xiaohong(CN)

Applicant(s): RESEARCH INSTITUTE OF PETROLEUM PROCESSING, SINOPEC (CN)

IPC Classification: C10F7/02

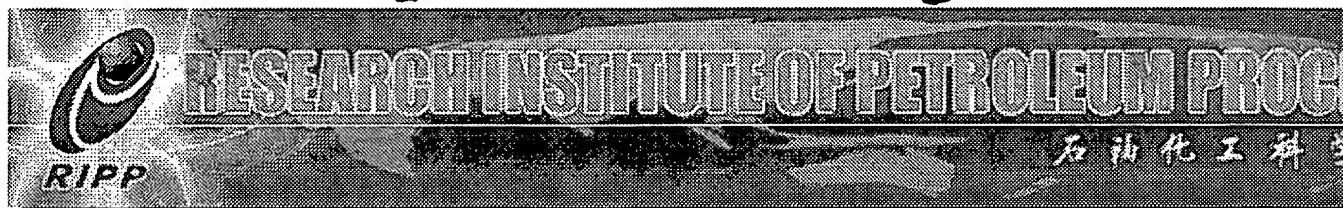
Abstract

A preparation method for pseudo-boehmite includes reacting sodium meta-alumina or sodium aluminate solution with carbon dioxide gas, gelation proceeds either batch-wise or continuous aging and separating the aluminum hydroxide solid products, washing and drying. The pH value in the course of gelation and to the final point were controlled within the range of 6~9.5, the gelation-forming or retention time is less than 40 minutes at 10~100°C. After gelation add an alkaline solution rapidly, the pH value of the slurry may rise to up to 9.5 and separates the solid and liquid rapidly then washing.

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A preparation method for pseudo-boehmite and gamma-alumina

□□

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